

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Polyamides

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which

5 we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to certain polyamide condensates and to their use in the treatment of shaped articles, particularly textile materials and films.

It has been found that the products obtained by the condensation of dicarboxylic acids with a mixture of a polyalkyleneoxy compound containing at least three primary amino groups with either an aliphatic, cycloaliphatic or aromatic diamine or with an aliphatic, cycloaliphatic or alkylcycloaliphatic amino acid and/or lactam, or with both, are useful for the treatment of shaped articles in order to impart valuable properties. The shaped articles may be composed of either natural or synthetic polymeric material.

25 Thus according to the present invention there are provided condensation products of (1) a dicarboxylic acid or amide-forming derivative thereof with (2) a mixture of (a) a polyalkyleneoxy compound containing at least three primary amino groups as herein-after defined and (b) an aliphatic, cycloaliphatic or aromatic diamine or an aliphatic, cycloaliphatic or alkylcycloaliphatic amino monocarboxylic acid and/or lactam or a mixture of the said diamine and amino monocarboxylic acid or lactam.

Instead of a single dicarboxylic acid, poly-

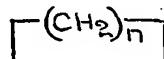
alkyleneoxy compound containing at least three amino groups, diamine or amino acid or lactam, mixtures of the said compounds may be used.

The dicarboxylic acids used in preparing the condensates are preferably aliphatic dicarboxylic acids of the formula:—



in which n represents zero or a positive integer from 1 to 10. Adipic acid is particularly suitable. Other suitable aliphatic dicarboxylic acids include oxalic acid, succinic acid, glutaric acid, sebacic acid and dodecanedioic acid.

Other suitable dicarboxylic acids are cycloaliphatic, alkylcycloaliphatic, aromatic and alkyl aromatic dicarboxylic acids. By cycloaliphatic dicarboxylic acids are meant acids containing an alkylene ring structure represented by the formula:—



wherein n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two carboxy groups to form the corresponding dicarboxylic acids. If aromatic acids are used the carboxy groups should not lie on adjacent carbon atoms of a ring system. Examples of such dicarboxylic acids include hexahydro - terephthalic acid,

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hexahydro - p - xylylenedicarboxylic acid, p - xylylenedicarboxylic acid, terephthalic acid and isophthalic acid.

5 The polyalkyleneoxy compounds containing at least three primary amino groups used in preparing the condensates are branched compounds containing three or more terminal amino groups joined directly or through suitable linking groups to 10 polyalkyleneoxy chains, which in turn are joined to a central nucleus having a functionality equal to the number of terminal amino groups. Such compounds are conveniently represented by the formula:—

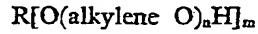


in which R represents the residue after the removal of the hydroxyl groups from a polyhydric alcohol of the formula  $R(OH)_m$ , Y represents a linking group, m is a positive integer which is at least 3 and n is a positive integer which is at least 2 and preferably at least 7. The alkylene groups in any one polyalkyleneoxy chain may be all the same or the chain may contain more than one kind of 25 alkylene group, for example it may contain a mixture of ethylene and propylene groups. The alkylene groups may contain from 2 to 12 carbon atoms but ethylene groups are particularly preferred.

30 The polyalkyleneoxy compounds containing at least three amino groups may be obtained from alkylene oxide condensates containing at least three hydroxyl groups, by replacement of the hydroxyl groups with amino groups in 35 known manner. Thus the said polyalkyleneoxy compounds may be obtained from an alkylene oxide condensate of the formula:—

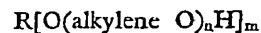


40 in which the symbols have the same significance as that defined above, by conversion of the hydroxyl groups into halogen atoms, for example into chlorine atoms by reaction with thionyl chloride, followed by reaction of the resulting polyhalogeno compound with 45 ammonia to give the corresponding polyamine compound; in this case Y represents an alkylene group which is the same as the alkylene group to which each hydroxyl group in the said alkylene oxide condensate was attached. Alternatively the polyalkyleneoxy 50 compounds may be obtained from an alkylene oxide condensate of the formula:—



55 in which the symbols have the same significance as previously, by reaction with acrylonitrile to give the poly -  $\beta$  - cyanoethyl ether, followed by reduction to the corresponding poly -  $\gamma$  - aminopropyl ether; in this case Y represents the group  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ .

Alternatively again the polyalkyleneoxy compounds may be obtained from an alkylene oxide condensate of the formula:—



by reaction with a 2 - aminomethyl - 3,4-dihydro - 2H - pyran derivative as described in our copending Application No. 5173/65, Serial No. 1,087,335; in which case Y represents a 2 - methylenetetrahydropyran - 6 - yl group.

The alkylene oxide condensates from which the polyalkyleneoxy compounds containing at least three amino groups are prepared may be obtained in known manner by reaction of an alkylene oxide, or a mixture of alkylene oxides, with a polyhydric alcohol containing at least three hydroxyl groups, optionally in the presence of an alkylene or acidic catalyst, for example potassium hydroxide or boron trifluoride. Suitable polyhydric alcohols include, for example, trihydric alcohols such as glycerol, trimethylolpropane, trimethylolethane and hexanetriol and polyhydric alcohols having more than three hydroxyl groups, such as pentaerythritol, erythritol, sorbitol, mannitol and sucrose.

Polyalkyleneoxy compounds which are preferred for use in preparing the condensates of the present invention are those containing three amino groups; accordingly it is preferred that the alkylene oxide condensates used in preparing the said polyalkyleneoxy compounds are derived from trihydric alcohols.

The alkylene oxides which are used in the preparation of the said alkylene oxide condensates are alkylene oxides having from 2 to 4 carbon atoms. Ethylene oxide and propylene oxide are particularly preferred.

The polyalkyleneoxy compounds containing at least three amino groups which are used in preparing the condensates of the present invention preferably have a molecular weight within the range 300 to 6000.

The aliphatic, cycloaliphatic or aromatic diamines used in preparing the condensates may be any aliphatic, cycloaliphatic or aromatic diamines, including alkyl cycloaliphatic and alkyl aromatic diamines. Particularly preferred, however, are aliphatic diamines having the formula:—



in which n represents a positive integer of from 2 to 12. Hexamethylene diamine is particularly suitable. Other suitable aliphatic diamines include ethylene diamine, nonamethylene diamine, decamethylene diamine, dodecamethylene diamine and  $\beta$  - methyl - hexamethylene diamine.

By cycloaliphatic diamines are meant diamines containing an alkylene ring structure:—

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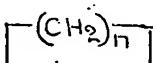
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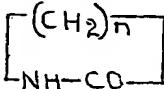
where n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two amino groups to form the corresponding diamines. If aromatic diamines are used the amino groups should not be on adjacent aroms. Examples of suitable cycloaliphatic and aromatic diamines are 1,3- and 1,4- diaminocyclohexane, p-xylylene diamine, p - phenylene diamine and p - tolylene diamine. The diamine may be used in the form of a salt with the dicarboxylic acid.

The aliphatic amino monocarboxylic acids or lactams used in preparing the condensates of the present invention are preferably  $\omega$ -amino aliphatic mono carboxylic acids and the derived lactams.

Particular compounds of this class may be represented by one of the formulae:—

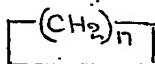


or



in which n is a positive integer from 5 to 11. Caprolactam is particularly suitable. Other suitable lactams include laurinolactam (dodecanolactam), enantholactam and capryllactam.

By cycloaliphatic amino monocarboxylic acids are meant amino monocarboxylic acids containing an alkylene ring structure represented by the formula:—



where n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by an amino and a carboxyl group respectively.

Alkylcycloaliphatic amino monocarboxylic acids used in preparing the condensates may have the amino and carboxyl groups attached either to the ring or to side chain carbon atoms.

Examples of cycloaliphatic and alkyl cycloaliphatic amino monocarboxylic acids include 4 - aminocyclohexanecarboxylic acid, 4 - aminomethylcyclohexanecarboxylic acid and 4 - aminocyclohexylacetic acid.

The ratio of the amount of dicarboxylic acid used in the preparation of the condensates to the combined amounts of the polyalkyleneoxy compound containing at least three amino groups and the aliphatic, cycloaliphatic or aromatic diamine may be varied within wide limits. The use of the stoichiometric equivalents will in general lead to the formation of hard, intractable, cross-linked polymers which are difficult to convert into a form suitable for application to a textile. When the condensates are to be used for this purpose it is accordingly preferred to use an excess of one or other of the reactants. It is also preferred that the ratio of the weight of the polyalkyleneoxy compound containing at least three amino groups of the combined weight of aliphatic, cycloaliphatic or aromatic diamine and aliphatic, cycloaliphatic or alkylcycloaliphatic amino acid and/or lactam should lie within the range 0.2 to 9.0.

The condensates of the present invention are conveniently prepared by mixing the components and heating them, for example at a temperature within the range 150°C. to 300°C. for from 30 minutes to 5 hours. Additives such as antioxidants, heat stabilisers, pigments and fillers which are stable under the polymerisation conditions may be included or these may be incorporated in the finished polymer.

In preparing the condensates there may be used instead of the dicarboxylic acids themselves certain derivatives of the dicarboxylic acids, for example the esters, especially the lower alkyl esters, and the halides of the said acids.

When an amino acid is used in place of a lactam it may be necessary to incorporate a 'flux', i.e. a substance which dissolves the components at the temperature of the reaction and which can be removed at the end of the reaction, e.g. by reducing the pressure and distilling out or by extraction with a solvent. An example of such a flux is o - phenylphenol. It may be desirable to carry out the condensation in an atmosphere of an inert gas such as nitrogen, or it may be desirable to carry out the condensation in the presence of a solvent such as water in a closed vessel under pressure.

The condensates are usually solids, often of a rubbery nature. Depending on the amount of polyalkyleneoxy compound containing at least three amino groups which is used, they show varying degrees of affinity for water, the affinity increasing with the proportion of alkyleneoxy groups in the molecule. Those condensates which are not soluble in water nevertheless become greatly swollen on immersion in water. Many of these are readily dispersible in aqueous media.

According to the present invention there is also provided a process for the treatment of shaped articles composed of natural or synthetic polymeric material which comprises applying to the said articles a condensate of the invention.

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A mixture of the said condensates may be used if desired.

Natural polymeric material which may be treated by the process of the present invention includes cellulose material and proteinaceous material such as keratin. Synthetic polymeric material which may be so treated includes polyamides such as nylon, including polymers and copolymers of acrylonitrile, cellulose esters such as cellulose triacetate and glass.

The shaped articles may be of any desired kind. They may be obtained from the polymeric material by any known shaping process for example by casting, moulding or extrusion. The process of our invention is particularly applicable, however, to filaments, fibres, felts and films and especially to textile materials comprising such filaments or fibres. Textile materials include rovings, yarns, non-woven webs and woven and knitted fabrics as well as filaments and fibres. Natural polymeric material may already be in fibrous form, as for example cotton and wool fibres, or may be converted into fibrous form as for example in the conversion of natural cellulose into the cellulosic rayons. Synthetic polymeric material may be converted into fibrous form by wet or dry spinning operations as may be appropriate.

The process of the invention may be used for example to treat cellulosic textile materials in order to modify the handle or improve the abrasion resistance. The process may also be used on cellulosic textile materials in conjunction with a crease-resisting agent such as a resin in order to impart a crease resist effect which is greater than that obtained with the crease resisting agent alone.

The process is particularly suitable for the treatment of shaped articles, especially textile materials and films, composed of hydrophobic synthetic polymeric material.

It is well known that shaped articles made from hydrophobic polymeric material besides having a very limited capacity for absorbing moisture become electrified readily when subjected to friction. These properties are disadvantageous in that the electrified articles readily attract dirt and dust. Moreover film composed of hydrophobic polymeric material which has become electrified is difficult to handle in that it becomes attracted to and clings to other articles. Further, textile materials composed of hydrophobic polymeric material which are used for clothing, besides having the disadvantage of soiling readily, tend to be uncomfortable in wear owing to the limited capacity for absorbing moisture. Such materials include those composed of polyamides, polymers and copolymers of acrylonitrile and cellulose triacetate.

Since the condensates of the present invention are readily dispersible in water, and may be soluble in water, it is convenient to apply

them to the shaped articles from an aqueous medium. If desired, however, a solution or dispersion in an organic solvent or in a mixture of an organic solvent with water may be used. The solution or dispersion may be applied to the shaped article by any suitable method, for example by dipping, impregnation or spraying, or by application with a brush, furnishing roller or squeegee. The application conveniently takes place at the ordinary temperature but if desired may take place at a moderately elevated temperature, for example at temperatures up to 50°C.

After application of the solution or dispersion the shaped article may be dried, if desired at the ordinary temperature, but conveniently at elevated temperatures up to about 120°C.

The amount of the condensation product applied to the shaped article may be varied within wide limits. In most cases, however, the amount applied lies within the range 0.1% to 5% of the weight of the shaped article.

In some cases it may be convenient to bake the shaped article after application of the condensation product so as to improve its fixation. For example the shaped article may be heated at a temperature within the range 120°C. to 220°C. for from 10 seconds to 30 minutes.

There may also advantageously be applied to the shaped article, in addition to the condensation product, a crosslinking agent or a resin precondensate and if desired a catalyst, which will react with the condensation product and assist in fixing the latter on the shaped article for example by reducing its solubility in water. Such materials may be applied together with the condensation product or they may be applied as a separate step, but their application should normally precede the baking treatment where such is used.

Suitable cross linking agents include aldehydes and dialdehydes such as formaldehyde, acrolein and glyoxal, capable of cross linking reactions; and cyanuric halides and dihalogenotriazine derivatives. Resin precondensates include the initial stage condensation products of formaldehyde with nitrogen compounds such as urea, thiourea, dicyandiamide, amides, amines, carbamates, aminotriazines, urons, ureins, ureides, imidazolidones, pyridones and triazines, especially the methylol derivatives of such compounds and the lower alkyl ethers of such methylol derivatives in which the alkyl groups contain from one to three carbon atoms; the methylol derivatives of nitrogen-containing polymers such as water-soluble urea/formaldehyde polycondensates, polyacrylamide and addition copolymers containing acrylamide, and the lower alkyl ethers of such methylol derivatives in which the alkyl groups contain from one to three carbon atoms; and

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5	polyacetals such as the acetal condensation products of aldehydes such as formaldehyde, acetaldehyde, glyoxal, malondialdehyde, succindialdehyde, adipaldehyde, hydroxyadipaldehyde and terephthalaldehyde with alcohols such as ethylene glycol, diethylene glycol, glycerol, pentaerythritol and dipentaerythritol, especially polyacetals of the type described in US Patent Specifications 2,785,947; 2,785,948; 2,785,949; 2,785,995; 2,785,996 and 2,786,081.	(i) polyhydric phenols such as pyrogallol, and esters of gallic acid; 65
10	If a catalyst is used it should be chosen so as to promote the reaction of the resin precondensate with itself or of the resin precondensate or cross-linking agent with the condensation product or with the shaped article or with both.	(ii) substituted monohydric phenols, particularly alkyl-, cyclo-alkyl-, aralkyl-, aryl-, and alkoxy- substituted phenols for example 2 - ( $\alpha$ - methylcyclohexyl) - 4,6 - dimethylphenol; 2,6 - di - t - butyl - 4 - methylphenol; 4 - benzyl - 2,6 - dihydroxy - methylphenol and 2,6 - di - t - butyl - 4 - methoxyphenol; 70
15	The catalyst may, for example, be an acid or an alkaline catalyst. In the case of resin precondensates, weakly acid substances or substances with liberate acid on heating are particularly suitable. As examples of such substances there may be mentioned, amongst others, organic acids such as oxalic acid; salts of weak bases and strong acids such as zinc chloride, the mineral acid salts of organic amines and especially ammonium salts such as ammonium sulphate and ammonium chloride; and substantially neutral substances which develop acidity on heating such as magnesium chloride and ammonium thiocyanate. Mixtures of such catalysts may be used if desired.	(iii) bis - phenols such as bis - (2 - hydroxy - 3 - ( $\alpha$ - methylcyclohexyl - 5 - methylphenyl)methane, 1,1 - bis - (2 - hydroxy - 3,5 - dimethylphenyl) - 1 - n - octylmethane and bis - (3 - t - butyl - 2 - hydroxy - 5 - methylphenyl)methane; 75
20	There may also be applied to the shaped article in conjunction with the condensates of the present invention other compounds which may serve to modify or enhance the effect achieved by the condensation product alone. Such compounds include, for example, hydroxyalkyl ethers of cellulose or starch.	(iv) sulphides such as dilaurylthiodipropionate, dioctyl - sulphide and bis - (5 - t - butyl - 4 - hydroxy - 2 - methylphenyl) sulphide; 80
25	There may also be applied to the shaped article in conjunction with the condensates of the present invention other compounds which may serve to modify or enhance the effect achieved by the condensation product alone. Such compounds include, for example, hydroxyalkyl ethers of cellulose or starch.	(v) dithiocarbamates such as sodium diethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dinonyldithiocarbamate, 2,6 - bis - (piperidinothiocarbonylthiomethyl) - 4 - methylphenol and 2,6 - di - t - butyl - 4 - diethylthiocarbamoylthiomethyl phenol; 85
30	By an antioxidant we mean a compound which prevents or retards the oxidation of organic compounds. Suitable antioxidants are those compounds which are already known as antioxidants for use in foodstuffs, in natural and synthetic rubbers, in lubricating oils and in polymers such as the polyolefines. Many compounds of this kind are already well known in the art. Among numerous publications in which such compounds are described there may be mentioned 'Autoxydation, Mesures de Prevention, Antioxydants' by M. Vignerol and 'Rubber Chemicals' by J. van Alphen (Elsevier Publishing Company, 1956).	(vi) dialkyldithiophosphates such as zinc dinonyldithiophosphate. 90
35	Particularly suitable for use as antioxidants in the process of our invention are compounds of the following classes—	After the application of the condensation product to the shaped article, and, if desired, the baking treatment, the shaped article may be rinsed in water and, if desired, washed in a hot solution of a detergent which may also contain an alkali, such as soda ash to neutralise any residual acidic catalyst. Finally the shaped article may be rinsed with water and dried. 95
40		Where the shaped article is a textile material the process of the invention may be applied before, in conjunction with, or after other chemical or mechanical finishing operations such as those used to confer resistance to shrinkage and creasing, modification of handle or surface lustre, water-repellency and optical brightness. 100
45		Shaped articles treated according to the present process are altered very little in appearance and retain their desirable characteristics. Textile materials composed of hydrophobic polymeric material retain their inherent characteristics, such as resistance to creasing or crushing, but usually they feel fuller and warmer to the touch. Their moisture absorbency is improved as a result of the treatment and their tendency to become electrified and to soil is diminished. These desirable properties are not easily destroyed by repeated washing and cleaning operations. 105
50		The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight— 110
55		EXAMPLE 1 25 Parts of the triamine prepared by reacting a condensate of glycerol with 18 moles of
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ethylene oxide successively with thionyl chloride and ammonia, 3.2 parts of adipic acid and 25 parts of caprolactam were heated in an atmosphere of oxygen-free nitrogen at 259°C. for 1½ hours. The mixture gelled after heating had been continued for 40 minutes. After cooling, the product was subjected to high-speed agitation with 300 parts of water for 2 hours. The resulting coarse dispersion was gravel-milled for 24 hours, giving a smooth stable dispersion containing 12.2% of solids.

A piece of a polyamide continuous filament fabric was impregnated with an aqueous composition prepared by the addition of 27.0 parts of the above dispersion and 0.8 part of a 20% aqueous non-ionic dispersion of the antioxidant bis - [2 - hydroxy - 3 - ( $\alpha$  - methylcyclohexyl) - 5 - methylphenyl]methane, to 72.2 parts of water. The fabric was then squeezed so as to retain 30% of its dry weight of liquor, dried at 120°C. for 45 seconds and subsequently heated at 200°C. for 30 seconds.

The resulting fabric, compared to an untreated control fabric, had a greatly reduced tendency to acquire charges of static electricity and possessed improved moisture absorbency.

#### EXAMPLE 2

25 Parts of the triamine prepared by reacting a condensate of glycerol with 23 moles of ethylene oxide successively with thionyl chloride and ammonia, 9.3 parts of adipic acid, 25 parts of caprolactam and 10 parts of water were heated in an atmosphere of oxygen-free nitrogen at 259°C. for 1 hour. The resulting gel after cooling was soaked in 300 ml. of water for several days and was then dispersed by high-speed agitation followed by gravel-milling. An extremely viscous dispersion was obtained having a solids content of 12.2%.

A piece of a polyamide continuous filament fabric was impregnated with an aqueous solution prepared by the addition of 27.0 parts of the above dispersion, 0.8 part of a 20% aqueous non-ionic dispersion of the antioxidant bis - [2 - hydroxy - 3 - ( $\alpha$  - methylcyclohexyl) - 5 - methylphenyl]methane, 0.7 part of a methylated urea-formaldehyde condensate prepared as described in Example 8 of British Patent Specification No. 953,754, and 0.3 part of ammonium chloride to 71.2 parts of water. The fabric was then squeezed so as to retain 30% of its dry weight of liquor, and dried at 140°C. for 1 minute.

The resulting fabric, compared to an untreated control fabric, possessed a much reduced tendency to acquire charges of static electricity and improved moisture absorbency. These effects were maintained after washing.

#### EXAMPLE 3

16 Parts of the triamine of Example 2, 1

part of adipic acid, 16 parts of caprolactam and 10 parts of water were heated gradually to 259°C. over 1 hour, water being allowed to distil off. The viscous melt was discharged into 300 parts of cold water and was dispersed therein by high-speed agitation followed by gravel-milling. The dispersion contained 8.0% of solids.

A piece of a polyamide continuous filament fabric was impregnated with an aqueous solution prepared by the addition of 41.0 parts of the above dispersion, 0.8 part of a 20% aqueous non-ionic dispersion of the antioxidant bis - [2 - hydroxy - 3 - ( $\alpha$  - methylcyclohexyl) - 5 - methylphenyl]methane 0.7 part of a methylated urea-formaldehyde pre-condensate prepared as described in Example 8 of British Patent Specification No. 953,754, and 0.3 part of ammonium chloride to 57.2 parts of water. The fabric was then squeezed so as to retain 30% of its dry weight of liquor, and dried at 140°C. for 1 minute.

The resulting fabric, compared to an untreated control fabric, possessed a much reduced tendency to acquire charges of static electricity and improved moisture absorbency. These effects were maintained after washing.

#### WHAT WE CLAIM IS :—

1. Condensation products of (1) a dicarboxylic acid or amide-forming derivative thereof with (2) a mixture of (a) a polyalkyleneoxy compound containing at least three primary amino groups as hereinbefore defined and (b) an aliphatic, cycloaliphatic or aromatic diamine or an aliphatic, cycloaliphatic or alkylcycloaliphatic amino monocarboxylic acid and/or lactam or a mixture of the said diamine and amino monocarboxylic acid or lactam.

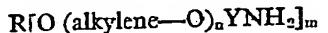
2. Condensation products as claimed in claim 1, wherein the dicarboxylic acid component is an aliphatic dicarboxylic acid of the formula :—



in which n represents zero or a positive integer from 1 to 10.

3. Condensation products as claimed in claim 2, wherein the dicarboxylic acid component is adipic acid.

4. Condensation products as claimed in any one of claims 1 to 3, wherein the polyalkyleneoxy compound containing at least three primary amino groups is a compound of the formula :—



in which R represents the residue after the removal of the hydroxyl groups from a polyhydric alcohol of the formula  $\text{R}(\text{OH})_m$ , Y represents an alkylene group, m is a positive

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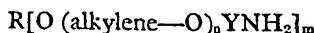
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integer which is at least 3 and n is a positive integer which is at least 2.

5. Condensation products as claimed in any one of claims 1 to 3, wherein the polyalkyleneoxy compound containing at least three primary amino groups is a compound of the formula: —



10 in which R represents the residue after the removal of the hydroxyl groups from a polyhydric alcohol of the formula  $R(OH)_m$ , Y represents a 2-methylenetetrahydropyran-6-yl group, m is a positive integer which is at least 3 and n is a positive integer which is at least 2.

15 6. Condensation products as claimed in claim 4 or claim 5, wherein the polyalkyleneoxy compound containing at least three primary amino groups is a compound of the formula herein stated in which m is 3.

20 7. Condensation products as claimed in any one of claims 1 to 6, wherein the polyalkyleneoxy compound containing at least three primary amino groups contains polyalkyleneoxy chains in which the alkylene groups are ethylene groups.

25 8. Condensation products as claimed in any one of claims 1 to 7, wherein the polyalkyleneoxy compound contains at least three primary amino groups has a molecular weight within the range 300 to 6,000.

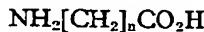
30 9. Condensation products as claimed in any one of claims 1 to 8, wherein the diamine component is an aliphatic diamine of the formula: —



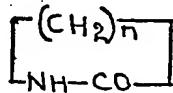
35 in which n represents a positive integer of from 2 to 12.

40 10. Condensation products as claimed in claim 9, wherein the diamine component is hexamethylenediamine.

45 11. Condensation products as claimed in any one of claims 1 to 10, wherein the amino acid component or lactam component is an  $\omega$ -aminoaliphatic carboxylic acid of the formula: —



or a lactam of the formula: —



50 in both of which formulae n is a positive integer from 5 to 11.

12. Condensation products as claimed in

claim 11, wherein the lactam component is caprolactam.

55 13. Condensation products as claimed in any one of claims 1 to 12, wherein the ratio of the weight of the polyalkyleneoxy compound containing at least three primary amino groups to the combined weight of the adipatic, cycloaliphatic or aromatic diamine and the aliphatic, cycloaliphatic or alkylcycloaliphatic amino acid and/or lactam lies between 0.2:1 and 9.0:1.

60 14. Condensation products according to claim 1 substantially as hereinbefore described, with particular reference to the foregoing Examples.

65 15. A process for the treatment of shaped articles composed of natural or synthetic polymeric material which comprises applying to the said articles at least one condensation product as claimed in any one of claims 1 to 14.

70 16. A process as claimed in claim 15, wherein the shaped article is a textile material.

75 17. A process as claimed in claim 15 or claim 16, wherein the synthetic polymeric material is a polyamide.

80 18. A process as claimed in any one of claims 15 to 17, wherein the condensation product is applied to the shaped article from an aqueous medium.

85 19. A process as claimed in any one of claims 15 to 18, wherein the amount of the condensation product applied to the shaped article lies within the range 0.1% to 5% of the weight of the shaped article.

90 20. A process as claimed in any one of claims 15 to 19, wherein the shaped article is heated, after application of the condensation product at a temperature within the range 120°C to 220°C for from 10 seconds to 30 minutes.

95 21. A process as claimed in any one of claims 15 to 20, wherein there is applied to the shaped article, in addition to the condensation product, a resin precondensate or a cross-linking agent for the polymeric material of the shaped article and/or for the condensation product and optionally a catalyst for promoting the reaction of the resin precondensate with itself or of the resin precondensate or cross-linking agent with the condensation product or with the polymeric material of the shaped article or both.

100 22. A process as claimed in claim 21, wherein the resin precondensate is an initial stage condensation product of formaldehyde with a nitrogen compound, or a lower alkyl ether of such a condensation product in which the alkyl group contains from one to three carbon atoms.

105 23. A process as claimed in claim 22, wherein a weakly acid substance or a substance which liberates acid on heating is used as a catalyst.

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24. A process as claimed in any one of claims 15 to 23, wherein the condensation product is applied to the shaped article in conjunction with an antioxidant.

5 25. A process as claimed in claim 24, wherein the antioxidant is a bis-phenol.

26. A process as claimed in claim 25, wherein the bis-phenol is bis - [2 - hydroxy-  
10 3 - ( $\alpha$  - methylcyclohexyl) - 5 - methyl- phenyl]methane.

27. A process for the treatment of shaped articles according to claim 15 substantially as hereinbefore described, with particular reference to the Examples.

28. Shaped articles whenever treated by 15 a process as claimed in any one of claims 15 to 27.

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